COMPREHENSIVE STUDY OF BASE ROCKS AS RAW MATERIAL FOR CERAMIC PRODUCTION

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Phase transformations proceeding in base rocks (metadiabases, metagabbro) upon heat treatment are considered. It is found that metadiabases can be used as fluxes in ceramic mixtures intended for high-temperature firing and in raw and fritted glazes as well.

Due to the need to expand the resources for construction materials in Belarus and the absence of high-quality raw materials on the Belarusian territory, the authors investigated the possibility of using base rocks (metagabbro, metadiabases) as a component in ceramic mixtures for high-temperature firing and in raw and fritted glazes.

The base rocks in Belarus are distributed within the limits of the crystalline foundation and are extracted in the Mikashevichskii stone quarry.

For our study we selected three types of rocks which significantly differ in their mineral (Table 1) and chemical (Ta-

ble 2) compositions: magnetite-free metadiabases, fine-grained and close-grained metadiabases, and metagabbro.

The materials were investigated using the petrographic, x-ray diffraction, and thermographic methods. The structure, mineralogic specifics, and the phase transformations of rocks in firing within the temperature interval of 950 – 1300°C were analyzed on samples made of powders.

As can be seen from the petrographic studies (Fig. 1), the fine- and close-grained metadiabases (rock sample 1) have a massive texture, the ophite structure, and consist of rounded tabular, or less often, prismatic plagioclase grains, short-prismatic and irregular-shaped grains of ordinary hornblende replaced by actinolite and hastingsite hornblende, biotite, and epidote. The latter mineral in the form of fine grains is found on plagioclase as well. Rare xenomorphic quartz

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TABLE 1

Material	Rock-forming minerals, vol.%							
	plagioclase	amphibole	biotite	epidote	quartz	microcline	magnetite	sphene
Fine- and close-grained metadiabase	50	37	5	3	2	–	2.6	0.4
Metagabbro	53	29	7	4	2	1	2.8	1.2
Magnetite-free metadiabase	44	47	4	3	1	–	–	1.0

TABLE 2

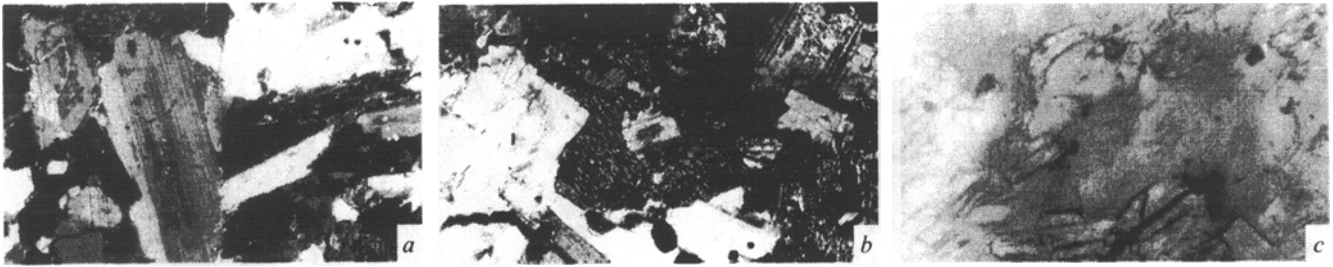| Material	Mass content, %											
	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	FeO	MgO	MnO	CaO	Na_2O	K_2O	SO_3	Calcination loss
Fine- and close-grained metadiabase	46.64 – 48.30	1.37 – 1.64	7.05 – 16.56	5.12 – 5.47	7.30 – 8.07	0.21 – 0.24	3.98 – 4.89	8.00 – 8.62	3.60 – 3.90	0.85 – 1.45	0.68 – 0.72	1.56 – 1.57
Metagabbro	54.14	0.57	13.64	2.89	6.10	0.15	6.66	9.39	2.88	1.45	0.30	1.82
Magnetite-free metadiabase	48.05	0.46	9.04	3.16	6.70	0.17	17.55	6.78	0.67	4.40	0.10	2.95

Fig. 1. Photos of the microstructure of base rocks (polarization microscope, ×35, nicol+): *a, b*, and *c*) rock samples 1, 2, and 3, respectively.

grains are present in the spaces between the plagioclase crystals.

The metagabbro (rock sample 2) has a medium-grained spotty structure determined by the presence of short-prismatic hornblende crystals constituting up to 50 – 70% of the rock volume. Microscopic analysis revealed the presence of monoclinal pyroxene grains and prismatic plagioclase crystals. The composition of plagioclase corresponds to andesine-labrador. Quartz is occasionally present in the spaces between the labrador grains.

The magnetite-free metadiabases (rock sample 3) are characterized by the ophite structure. The bulk of the rock consists of chaotically oriented laths and tabular, less often irregular plagioclase grains with a relic twin structure and aggregates of short-prismatic, not definitely edged ordinary hornblende grains which are often replaced by actinolite, edenite, and hastingsite hornblende. The amphibole contains occasional fine inclusions of epidote, sphene, apatite, and rarely, magnetite and pyrite. Occasional quartz grains are found. These rocks have a greenish-gray color and contain a large amount of amphibole.

After firing at a temperature of 950 – 1000°C, the composition and the structure of the samples change to some extent. The hornblende-related diffraction maxima decrease. This is possibly related to a change in the structure of the mineral determined by the transition of Fe^{2+} to Fe^{3+} on removal of hydrogen from the hornblende lattice [1], which is supported by the DTA data. The thermograms register an endothermic effect in the temperature region of 440 – 570°C, which is caused by the oxidation of structural iron forming part of hornblende and biotite [2]. Free hematite is formed in this manner. All samples acquire a red-brown color which becomes more intense with increase in temperature.

At a firing temperature of 1000°C, the diffraction maxima corresponding to plagiolase and biotite in the x-ray diffraction patterns of rock sample 1 virtually do not change. The hastingsite hornblende (a mineral of the amphibole group) starts disintegrating. Water removal and the destruction and amorphization of the above mineral result in looseness of the sample microstructure. The decomposition of actinolite within the temperature interval of 950 – 1020°C does not cause significant changes in diffraction patterns. The samples do not sinter.

At a temperature of 1100°C, a sharp decrease in the intensity of the hornblende and biotite lines is observed in the
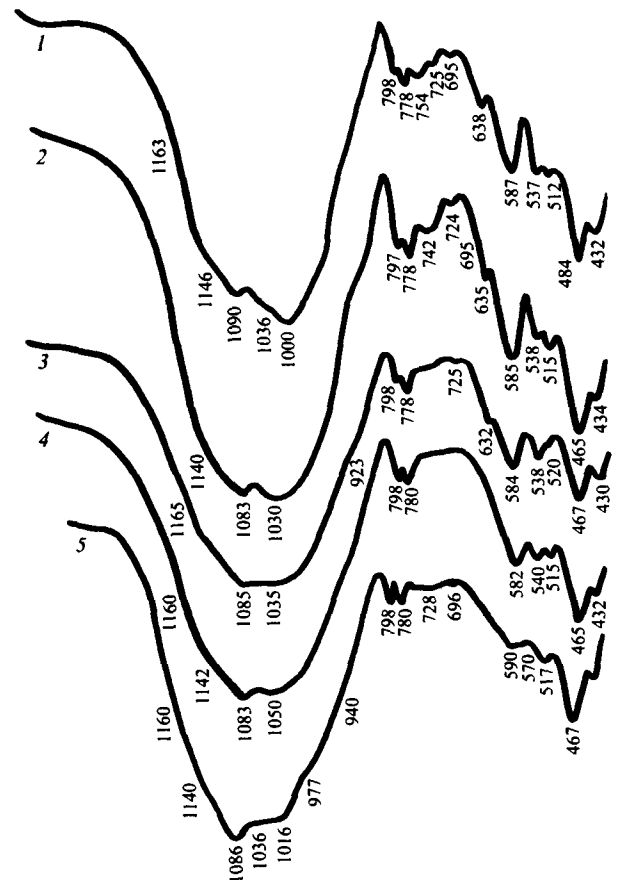

Fig. 2. IR spectra of natural and fired metadiabases: *1*) natural metadiabase; *2, 3, 4*, and *5*) metadiabases heat treated at temperatures of 1000, 1100, 1200, and 1300°C, respectively.

diffraction patterns. Hypersphene emerges, and the amount of hematite substantially increases. According to the DTA data, the formation of hypersphene occurs on destruction of the rock-forming minerals within a temperature range of 1050 – 1150°C with simultaneous removal of chemically bound water. Partial sintering of the samples takes place.

A further increase in temperature up to 1150°C results in the appearance of the liquid phase in the samples. The samples were found to contain plagioclase grains and crystals of hematite and hypersphene (a mineral of the pyroxene group). The water absorption of the samples is 11.2 – 15.0%. The
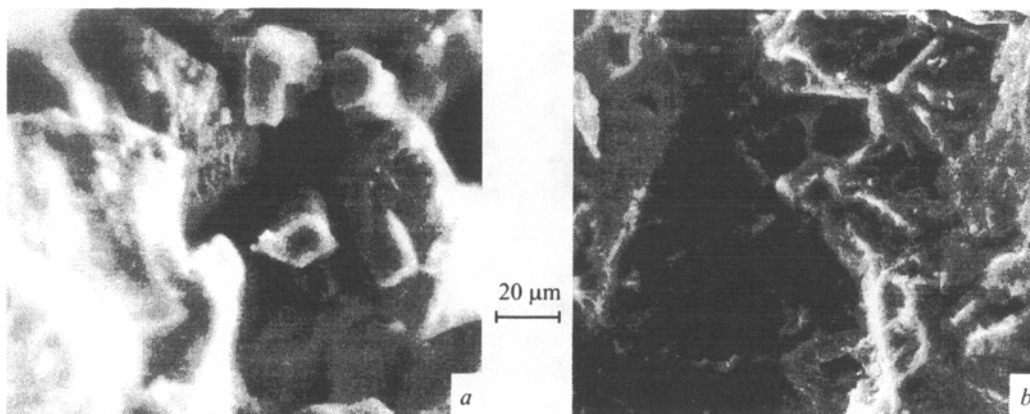
Fig. 3. Electron microscopic photos of metadiabase fired at temperatures of 1150°C (*a*) and 1180°C (*b*).

poor sintering of the samples at the specified temperatures can be attributed to the solid-phase sintering mechanism and a small quantity of the emerging melt. A further fusion of the plagioclase grains takes place at a temperature of 1180 – 1200°C. Hypersphene completely passes over to the melt, and hematite is present. The samples vitrify and start swelling. They are characterized by near-zero values of water absorption and sealed porosity. At a temperature of 1200°C, the samples are x-ray amorphous.

The IR spectra (Fig. 2) of the initial and heat-treated metadiabase (rock sample 1) confirm the results of the x-ray phase and petrographic analysis. The absorption bands with strong maxima in the region of 1000 cm^{-1} and two weaker ones between 1190 and 1052 cm^{-1} in the initial rock sample correspond to the amphibole spectra. The most intense absorption bands for plagioclases, which are characterized by the silicon-oxygen cell in the form of $[SiO_2]^{3\infty}$, are observed within the region of 1180 – 1190 cm^{-1}. The singular stretching vibrations of the $[SiO_4]$ group for metadiabases with a wave frequency of 960 – 1190 cm^{-1} are manifested as single bands, which is indicative of the presence of asymmetric discrete silicon-oxygen tetrahedrons. The band of 520 – 512 cm^{-1} corresponds to the stretching vibrations of the $[Fe^{3+}O_4]$ and $[Mg^{2+}O_4]$ groups, and the bands of 434 – 432 cm^{-1} relate to the stretching vibrations of the $[Fe^{2+}O_6]$ and $[Fe^{3+}O_6]$ groups. The amount of Fe^{3+} and Al^{3+} cations in four coordination, which act as structure formers, is much lower than that of Fe^{3+}, Al^{3+}, Mg^{2+}, Fe^{2+} in six coordination, which is indicated by the depth of the bands in the ranges of 700 – 800 and 400 – 500 cm^{-1}.

The observed redistribution of the absorption spectra corresponding to the stretching vibrations of $[SiO_4]$ group points to the disintegration of the initial material structure in heating the samples. The shift of the absorption bands from 950 to 923 cm^{-1} and the intensification of the band in the region of 1080 cm^{-1} corresponding to O – Si – O and Si – O – Si asymmetric stretching vibrations are determined by the destruction of the band-shaped amphibole structure and formation of chain-shaped pyroxenes and skeletal plagioclases. The destruction of amphiboles in heating is

confirmed by the disappearance of the absorption band near 750 cm^{-1}.

The diffusion of the absorption bands with increase in heat treatment temperature indicates as well an increase in the amount of the vitreous phase in the sample [2].

The study of the phase transformations in rock sample 2 in firing revealed that hastingsite hornblende decomposes at a temperature of 1050 – 1120°C, and biotite decomposes at 1100 – 1180°C. The content of pyroxene increases with increasing temperature. The quantity of plagioclase passing into the melt is insignificant. At temperatures about 1200°C, the liquid phase appears in an amount sufficient for the dissolution of the initial and newly formed crystalline mineral phases. According to the data of the x-ray phase analysis, the samples become amorphous at 1220 – 1250°C.

In rock sample 3, the destruction of the crystal lattice of actinolite in firing occurs at 980 – 1050°C, and the destruction of hastingsite hornblende takes place at 1050 – 1200°C. The processes of formation of hematite and minerals belonging to the groups of pyroxene and plagioclase proceed simultaneously with the destruction of biotite and hornblende. The melting temperature interval for these samples comprises 50°C and lies between 1250 and 1270°C.

As can be seen, the processes which have a strong influence on the degree and nature of structure formation are shifted in rock samples 2 and 3 are shifted by 30 – 50°C to higher temperature region. This is caused by significant differences in the chemical and mineralogical compositions of the initial minerals: the total content of Fe_2O_3 + FeO and NaO + K_2O in rock sample 1 is higher by 3.70 and 1.02%, respectively, than in rock sample 2 and higher by 1.23 and 0.85% than in sample 3. Table 2 shows that the samples also differ in the content of Al_2O_3, MgO, and other components.

Figure 3 shows the electron microscopic studies of samples fired at temperatures of 1150 and 1180°C. The structure of fine- and close-crystalline metadiabase fired at a temperature of 1150°C is composed of large conglomerates whose main elements are fused tabular crystals apparently belonging to plagioclases and pyroxenes, whose size varies from 5

to 20 μm. The channel-forming pores are of irregular shape and can be very large, up to 40 – 60 μm.

At a temperature of 1180°C, the nature of the structural elements in the fine- and close-grained metadiabases changes significantly. The material almost completely loses its crystallographic contours. Only single highly fused tabular crystals of small size are present. The pores are predominantly isometric, less often extended, and are interconnected by narrow channels. The pore size is 5 – 40 μm.

Thus, the performed investigations show that the base rocks can have a fusing effect and act as fluxes in ceramic mixtures in high-temperature firing.

The possibility of substituting metadiabases for traditional raw materials such as pegmatites and feldspars was investigated on model mixtures which contained (wt.%): 10 refractory clay, 65 concentrated kaolins, and 25 pegmatites or metadiabases.

The model compositions were prepared in a ball mill by wet grinding up to a residue of 1.5 – 2.0% on a No. 0063K sieve. The samples were molded by semidry pressure (moisture 7 – 8%) at a specific pressure of 35 – 40 MPa and fired in electric laboratory furnaces with holding at the maximum temperature of 1200°C for 15 min.

The analysis of the results shows that metadiabases have a stronger fluxing effect than pegmatite. Thus, the water absorption of the sample with pegmatite was 4.8%, and that of the mixture with metadiabase was 2%. In using metadiabase, shrinkage grows up to 6.2% against 4.2% in the sample containing pegmatite, and the bending strength increases to 52.9 MPa against 39.4 MPa.

The samples containing metadiabases have a reddish-brown color.

The phase composition of the samples is shown in Fig. 4. The x-ray structural analysis revealed that the main crystalline formations in the samples are quartz, plagioclase, mullite, and hematite. The x-ray patterns of the mixtures containing pegmatite are characterized by intense maxima corresponding to mullite and quartz, and plagioclase is virtually absent here. Upon introduction of metadiabase, the processes of plagioclase, mullite, and hematite crystallization and dissolution of quartz are intensified. The morphological structure of the samples is dense and monolithic. The mixtures containing metadiabases exhibit clusters of very small fused crystal formations 6 – 10 μm in size. The structure of the mixtures containing pegmatite consists mostly of larger crystals. All samples contain pores whose size does not exceed 5 – 10 μm.

Thus, metadiabase in the high temperature region is a more efficient flux than the traditionally used pegmatite.

The possibility of using rocks for glaze synthesis in the $R_2O - RO - B_2O - Al_2O_3 - (Fe_2O_3)FeO - SiO_2$ system was investigated as well ($R_2O = Na_2O + K_2O$; $RO = CaO + MgO$).

The frits were melted in crucibles in an open flame gas furnace at a temperature of 1350 – 1400°C with holding at the maximum temperature for 1 – 1.5 h until a homogeneous glass melt was obtained.
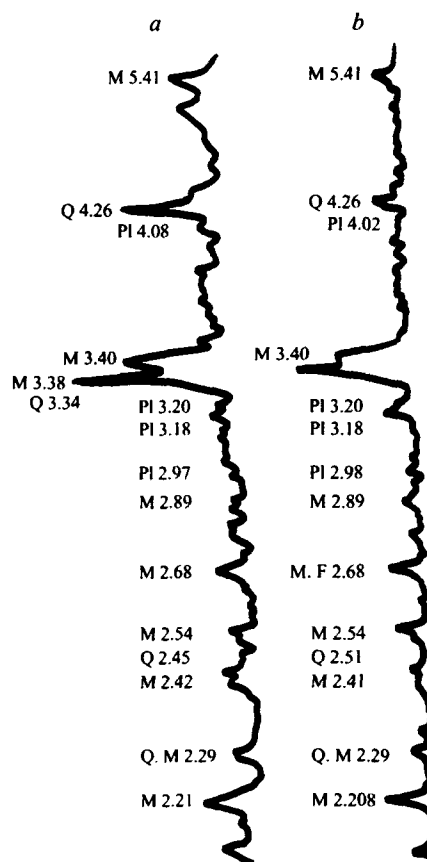

Fig. 4. X-ray patterns of model mixtures based on pegmatite (a) and metadiabase (b) fired at 1200°C: Pl) plagioclase, Q) quartz; M) mullite; F) hematite.

The raw and fritted glazes were prepared by joint wet grinding of all components with introduction of 4 – 6% (above 100%) refractory clay of the VGO grade until a residue of 0.05% remained on a No. 0063K sieve.

The fritted and raw glazes of the optimum compositions made it possible to obtain high-quality colored coatings with a good spread and mirror-like luster in the temperature region of 950 – 1000°C. The color of the coatings ranged from red-brown and pale green to dark, almost black shades. It was found that the amount of diabase in the glaze composition can vary from 30 to 60%.

The performed comprehensive research revealed the possibility and expediency of using metadiabase as a component in ceramic mixtures for high-temperature firing and in fritted and raw glazes. This makes it possible to substantially expand the available raw material resources for ceramic industry.

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